

**Attempts to Prepare  $I(OSO_2F)_5$ .**—Unsuccessful attempts were made by two methods to prepare iodine(V) fluorosulfate. In one procedure iodine was allowed to react with  $S_2O_8F_2$  in relative proportions of about 1 to 7 at 95°, 115°, or 130°. Oxygen and  $S_2O_8F_2$  were found as products. After removal of the volatile substances, a yellow material remained in which the oxidation state of iodine was close to 5 and the ratio of fluorosulfate to iodine (as shown by the ratio, weight of product to weight of iodine) was from 2:1 to 3:1. When the reaction occurred at 60° in an n.m.r. tube, even after 72 hr. the principal product was  $I(OSO_2F)_3$  and the excess  $S_2O_8F_2$  had not decomposed. In the second procedure a mixture of sulfur trioxide with  $IF_3(OSO_2F)_2$  in a molar ratio of 7 to 1 was held at 50 to 55° for several hours. A yellow oil was produced in which the oxidation state of iodine

was 5, but the weight was much less than for iodine(V) fluorosulfate. The products included  $S_2O_8F_2$  and  $S_2O_5F_2$  (identified by infrared spectra). When the reactants were held together in an n.m.r. tube for 8 days the final spectrum indicated that a part of the fluorine originally bound to iodine had been removed but that the number of  $SO_2F$  groups attached to iodine had not increased. Probably an iodine(V) oxyfluorosulfate was formed.

**Acknowledgments.**—This work was performed under contract with the Office of Naval Research. The authors appreciate the assistance of B. J. Nist for running n.m.r. spectra and thank Professor Howard Clark of the University of British Columbia for his assistance in using a Gouy balance at that institution.

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## The Reaction of Diphenylchlorophosphine with Ammonia-Free Chloramine

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Received September 24, 1964

The reaction of diphenylchlorophosphine with ammonia-free chloramine in diethyl ether yields  $(C_6H_5)_2P(NH_2)(Cl)NHP(Cl)_2(C_6H_5)_2$ . When this compound is pyrolyzed  $[(C_6H_5)_2PN]_2$  and  $[(C_6H_5)_2PN]_4$  are formed in high yield. Hydrolysis gives  $(C_6H_5)_2P(O)NHP(O)(C_6H_5)_2$  and  $(C_6H_5)_2P(O)NP(Cl)(C_6H_5)_2$ . Ammonolysis gives the known compound  $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$ .

In a previous paper<sup>1</sup> the reaction of diphenylchlorophosphine with a gaseous mixture of chloramine and excess ammonia was described. Since the postulated course of this reaction involved ammonolysis of the halophosphine, followed by addition of the chloramine to the aminophosphine, and the subsequent condensation to the phosphonitrile by loss of ammonium chloride, it was considered of interest to study the reaction of diphenylchlorophosphine with chloramine in the absence of ammonia and to compare the intermediates and final products obtained with those obtained when the presence of ammonia brings about ammonolysis of the phosphorus-halogen bond. Furthermore, the complete absence of ammonia or other strong base in the system should make it possible to draw interesting implications concerning the nature of the chloramination reaction.

### Experimental

**Materials.**—Diphenylchlorophosphine, obtained from the Victor Chemical Works, was redistilled under vacuum immediately before use.

The gaseous mixture of chloramine and excess ammonia was produced by the gas phase reaction of chlorine with an excess of ammonia in a generator of the type described by Sisler and Omietanski<sup>2</sup> and was freed of ammonia using anhydrous copper sulfate, as described below.

All solvents were redistilled and kept over an appropriate drying agent, usually calcium hydride.

Handling operations were carried out in either a drybox or a dry polyethylene bag, under an atmosphere of dry nitrogen. All reaction apparatus was flushed with dry nitrogen before use.

Elementary analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Nitrogen and chlorine analyses were also checked by the authors. All melting points are uncorrected.

**Preparation of Anhydrous Ammonia-Free Chloramine Solutions.**—A gaseous mixture of chloramine and ammonia, produced by the gas phase reaction of chlorine with an excess of ammonia,<sup>3</sup> was introduced into the solvent, cooled in an ice-salt bath, until approximately the desired concentration of chloramine was obtained. The solution was warmed to room temperature to decrease the ammonia content and then passed through a column of anhydrous copper sulfate. The copper sulfate had previously been dried at over 500° and the column dimensions were chosen with regard to the volume of solutions used, a column approximately 2 in. in diameter and 3 in. long being sufficient for 250 ml. of solution using a flow rate of about 50 ml./min. or greater. The fast flow rate is desirable since the chloramine slowly reacts with the copper sulfate. This is shown by the observation of a green color in the column below the deep blue region of ammonia absorption, by the evolution of a colorless, odorless gas, presumably nitrogen, and by a decrease in the chloramine content of the solution during its passage through the column.

The absence of ammonia in the effluent solution was shown by extracting samples of that solution with water and measuring the pH of the aqueous extract. In each case pH values between 6.5 and 7.0 were obtained.

The chloramine solutions were allowed to stand over Linde Molecular Sieve; Type 4A was used since this absorbs water but not ammonia or chloramine. The solutions were sampled at regular time intervals. The chloramine content was determined by pipetting a 10-ml. sample into a mixture of 25 ml. of acidified potassium iodide solution and 10 ml. of chloroform. The mixture was then titrated with standard sodium thiosulfate solution, with vigorous shaking, until the color in the chloroform layer was discharged. In all solvents tried (diethyl ether, benzene, and tetrachloroethane) the concentration of chloramine decreased with time. Data for a typical experiment in diethyl

(1) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

(2) H. H. Sisler and G. Omietanski, *Inorg. Syn.*, **5**, 91 (1957).

(3) H. H. Sisler and R. Mattair, *J. Am. Chem. Soc.*, **73**, 1619 (1951).

ether at 25° (time in minutes, molarity of chloramine) are as follows: 0, 0.058; 15, 0.049; 30, 0.043; 45, 0.041; 90, 0.039; 150, 0.038; and 1560, 0.035. Typical data for a solution of chloramine in benzene at 25° are: 0, 0.089; 15, 0.085; 34, 0.082; 180, 0.080; and 1275, 0.070. Typical data for a solution of chloramine in tetrachloroethane at 25° are: 0, 0.044; 50, 0.028; 100, 0.011; and 300, 0.000.

Diethyl ether solutions as concentrated as 0.6 *M* in chloramine were obtained, but the maximum concentrations of chloramine in benzene and in *sym*-tetrachloroethane that could be obtained by our method were about 0.2 and 0.1 *M*, respectively.

**Reaction of Diphenylchlorophosphine with Chloramine.**—The following is a description of a typical experiment: 5 ml. of diphenylchlorophosphine (0.027 mole) was very slowly added to a well-cooled, well-stirred, ammonia-free solution of chloramine (0.031 mole) in 200 ml. of diethyl ether. A white precipitate formed immediately. Stirring and cooling were continued for 10 to 15 min. after the addition of diphenylchlorophosphine was complete. The solid reaction product was filtered under an atmosphere of dry nitrogen; yield, 6.8 g. of compound I, m.p. 99–104°. A portion of the filtrate was analyzed for chloramine and found to contain the equivalent of 0.002 mole of chloramine in 200 ml. of ether. Consequently 0.027 mole of diphenylchlorophosphine had, within experimental error, reacted with an equivalent amount of chloramine.

The product tends to lose hydrogen chloride very easily and attempts at recrystallization always gave viscous oily substances of indeterminate composition and varying melting points.

A number of experiments were also carried out using excess diphenylchlorophosphine. Examination of the filtrate from these experiments showed only the presence of diphenylchlorophosphine, showing that all the chloramine had been consumed.

**Identification of Compound I.**—*Anal.* Calcd. for  $(C_6H_5)_2P(NH_2)(Cl)_2$ : C, 52.97; H, 4.44; N, 5.14; Cl, 26.06; P, 11.38. Found: C, 48.07; H, 5.22; N, 7.72; Cl, 28.85; P, 10.26. The poor analysis obtained results from the unstable character of the compound  $(C_6H_5)_2P(NH_2)(Cl)_2$ . Tessi and Douglas<sup>4</sup> found that compounds of the formula  $R_2P(NH_2)(Cl)_2$  obtained by the reaction of molecular chlorine with aminophosphine evolve hydrogen chloride even at -30°. Thus, our results are in accord with theirs if we presume that the product of the chloramination of diphenylchlorophosphine is analogous to that of the chlorination of the aminophosphine.

If the reaction of chloramine with diphenylchlorophosphine is carried out using an excess of diphenylchlorophosphine, stirring for at least 1 hr. after the addition of diphenylchlorophosphine is complete, and drying the product *in vacuo* overnight, a product, compound II, m.p. 83–85°, is obtained. *Anal.* Calcd. for  $(C_6H_5)_2P(Cl)(NH_2)NHP(Cl)_2(C_6H_5)_2$ : C, 56.70; H, 4.52; N, 5.51; Cl, 20.97; P, 12.21. Found: C, 55.4; H, 5.55; N, 5.87; Cl, 20.56; P, 12.39.

The infrared spectra of both compounds showed peaks attributable to monosubstituted phenyl at 3185  $cm^{-1}$ , to NH at 3085  $cm^{-1}$ , to tetracoordinated phosphorus with a phenyl linkage at 1125  $cm^{-1}$ ,<sup>5</sup> to phosphorus-phenyl at 1430  $cm^{-1}$ . A band at 940–960  $cm^{-1}$  is also found in the infrared spectrum for compound II. This band has been attributed to the P-NH-P group.<sup>6</sup> It is, therefore, suggested that the reaction between diphenylchlorophosphine and chloramine proceeds in two stages; first, the formation of  $(C_6H_5)_2P(NH_2)Cl_2$ , and then intermolecular loss of hydrogen chloride to form  $(C_6H_5)_2P(Cl)(NH_2)NHP(Cl)_2(C_6H_5)_2$ .

**Hydrolysis of Compound II.**—Product II was heated to 100° in the presence of moist air for 2 hr. and extracted with hot benzene. On cooling a crystalline solid IV, m.p. 267–270°, was obtained. *Anal.* Calcd. for  $(C_6H_5)_2P(O)NHP(O)(C_6H_5)_2$ : C, 69.00; H, 5.03; N, 3.35; P, 14.85. Found: C, 67.71; H, 5.31; N, 3.41; P, 14.03; Cl, traces only. The infrared spec-

trum of this product showed peaks at 1330, 1310, 1190, 1120, 1110, and 935  $cm^{-1}$  agreeing with those given by Paciorek<sup>7</sup> and the melting point is that given by Korshak, *et al.*,<sup>8</sup> for the compound  $(C_6H_5)_2P(O)NHP(O)(C_6H_5)_2$ . Extraction of the hydrolyzed mixture with chloroform, rather than benzene, and the addition of diethyl ether precipitated product III, m.p. 282–284°, of similar infrared spectrum to the previous hydrolyzed product with peaks at 1330, 1310, 1120, and 1110  $cm^{-1}$  but missing the P-NH-P band at 935  $cm^{-1}$ . However, a small band attributable to the P-N=P linkage is found at 1175–1220  $cm^{-1}$ . *Anal.* Calcd. for  $(C_6H_5)_2P(O)NP(Cl)(C_6H_5)_2$ : C, 66.07; H, 4.58; N, 3.21; Cl, 8.14; P, 14.22. Found: C, 65.57; H, 4.98; N, 3.59; Cl, 8.01; P, 14.12.

**Pyrolysis of Compound II.**—A typical pyrolysis experiment was conducted as follows: 3.0 g. of compound II was heated under vacuum to 300° for 24 hr. The mixture was allowed to cool and was then refluxed with dry benzene and the insoluble matter filtered off (residue 0.23 g., m.p. 300–308°). By carefully reducing the volume of filtrate by evaporation under vacuum, 0.83 g. of product VII, m.p. 318–319°, and 0.36 g. of product VI, m.p. 226–229°, were obtained. Complete evaporation of the remaining benzene left a brown substance, m.p. 203–210° (0.32 g.).

The two products melting, respectively, at 318–319 and 226–229° were identified by infrared spectra and mixture melting points with authentic samples to be diphenylphosphonitrilic tetramer (VII) and trimer (VI), respectively. The products melting at 300–308 and 203–210° were not characterized. The yields of tetramer and trimer were 61.9 and 20.0%, respectively, based on the amount of diphenylchlorophosphine originally used.

All the products of the pyrolysis reaction showed the characteristic P-N=P peaks between 1100 and 1250  $cm^{-1}$  in their infrared spectra.

**Ammonolysis of Compound II.**—Compound II (2.0 g.) was treated with two successive 100-ml. portions of liquid ammonia. The ammonia was allowed to evaporate and the residue was refluxed with *sym*-tetrachloroethane. The insoluble ammonium chloride was filtered off and the filtrate allowed to cool to room temperature. On addition of *n*-hexane a white solid V, m.p. 239–241°, was obtained. By comparison with an authentic sample using mixture melting point and infrared spectra, this was identified as pure  $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$ .<sup>1</sup> *Anal.* Calcd.: N, 9.3; Cl, 7.85. Found: N, 9.7; Cl, 8.03.

Product V has also been prepared from  $(C_6H_5)_2P(Cl)NP(NH_2)(C_6H_5)_2$  (VIII).<sup>1</sup> A sample of VIII (0.5 g.) in *sym*-tetrachloroethane (10 ml.) was treated with excess dry gaseous ammonia and then with excess dry gaseous hydrogen chloride. The solution was filtered and *n*-hexane added; 0.3 g. of solid was obtained, giving an infrared spectrum and melting point identical with those of V.

## Discussion

The results reported above clearly establish the sequence of reactions shown in Scheme I.

The presence in the infrared spectrum of I of the characteristic infrared band at 1125  $cm^{-1}$  indicates that the phosphorus atom is tetravalent so that one may reasonably assign the structure  $[(C_6H_5)_2P(NH_2)Cl]-Cl$  to this product. The insolubility of I in benzene and ether is in agreement with this structure. The presence of this same band in the structure of II indicates that at least one of the phosphorus atoms is tetravalent. The question as to whether or not both phosphorus atoms are tetravalent rather than pentavalent remains unresolved. However, a reasonable

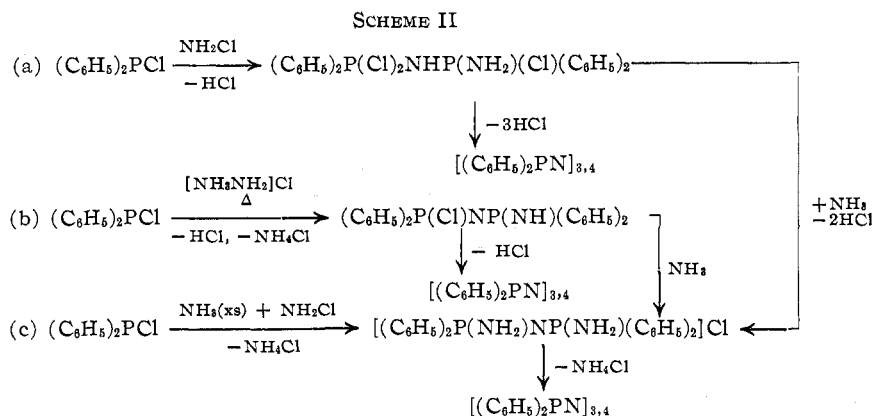
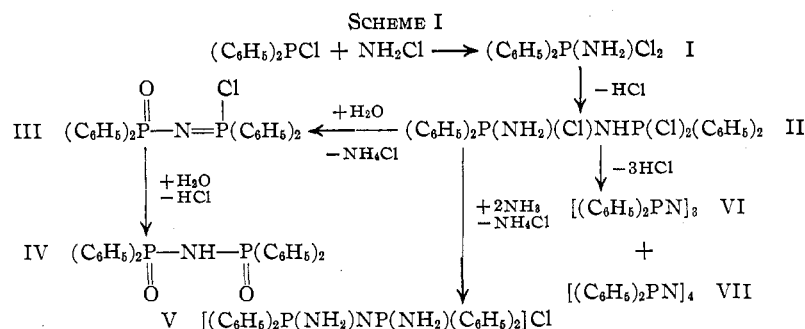
(4) G. Tessi and C. M. Douglas, Naval Weapons Report 539 (Oct.–Dec. 1960).

(5) W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

(6) E. Steger, *Chem. Ber.*, **94**, 266 (1961).

(7) K. L. Paciorek, *Inorg. Chem.*, **3**, 96 (1964).

(8) V. V. Korshak, I. A. Gribova, T. V. Artamonova, and A. W. Bushmarina, *Vysokomolekul. Soedin.*, **2**, 377 (1960).



assumption for the structure of II would be  $[(\text{C}_6\text{H}_5)_2\text{P}(\text{Cl})\text{NHP}(\text{NH}_2)(\text{C}_6\text{H}_5)_2]\text{Cl}_2$ .

It is interesting to note that the virtually quantitative formation of the compound  $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)\text{Cl}]\text{Cl}$  by the direct reaction of chloramine with  $(\text{C}_6\text{H}_5)_2\text{PCl}$  in the absence of any base stronger than  $(\text{C}_6\text{H}_5)_2\text{PCl}$  or diethyl ether is further evidence against the necessity for assuming the existence of the  $\text{NHCl}^-$  species as an intermediate in the chloramination process.<sup>9</sup>

It is interesting to note that the work reported herein,

(9) G. Yagil and M. Anbar, *J. Am. Chem. Soc.*, **84**, 1797 (1962).

along with that previously reported in this laboratory,<sup>1</sup> has established three related procedures for converting  $(\text{C}_6\text{H}_5)_2\text{PCl}$  to  $[(\text{C}_6\text{H}_5)_2\text{PN}]_3$  and  $[(\text{C}_6\text{H}_5)_2\text{PN}]_4$ .

In each case an intermediate was isolated, each one bearing an interesting relationship to the others, as the reactions shown in Scheme II indicate.

**Acknowledgment.**—We are pleased to acknowledge the partial support of the work reported herein by the National Science Foundation through a research grant (NSF G-P-1600) to the University of Florida.

CONTRIBUTION FROM SHIONOGI RESEARCH LABORATORY,  
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## Steric Effects in Tris(N-boryl-2-pyridylamino)borane and Its Derivatives

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Received August 17, 1964

The presence of three B←N coordinate bonds in tris(N-boryl-2-pyridylamino)boranes was confirmed by the chemical shift of the <sup>11</sup>B nuclear magnetic resonance spectrum as well as by the B-H stretching frequency of tris(N-boryl-2-pyridylamino)borane itself. The reactions between boron trichloride and some ring-substituted 2-aminopyridines were examined to appraise the importance of the coordinate bonds in the formation of this series of compounds. The reactions indicated that the substituent on the 3-position of pyridine prevented the formation of the B←N coordinate bonds and of the framework, and that the coordinate bonds are indispensable.

In an earlier paper<sup>1</sup> dealing with the reaction between boron trichloride and 2-aminopyridine followed by an appropriate Grignard reaction, it was shown that the reaction afforded a new type of compounds as shown in

Figure 1. The three coordinate bonds between ring nitrogen and boryl boron atoms were deduced from the electronegativity of boron and steric requirements. The present paper has aimed first, at confirming the presence of the three boron-nitrogen coordinate bonds and second, at evaluating the importance of the B←N coordinate bond in formation of this series of compounds.

(1) H. Watanabe, K. Nagasawa, T. Totani, T. Yoshizaki, and T. Nakagawa, "Boron-Nitrogen Chemistry," *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1964, p. 116.